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EP 0 419 669 A1

THERMOSETTING COMPOSITION.

A thermosetting composition comprising a hydroxylated resin, a hydrolyzable silyl compound polymer, a hydrolyzable silicon compound, and a curing catalyst gives a coating material free from the problem of malodor, and a coating film prepared therefrom is improved in adhesion, solvent resistance and hardness.

TERMOSETTING COMPOSITION

TECHNICAL FIELD

The present invention relates to a thermosetting composition which is used for various coatings for outer walls of buildings, automobiles, industrial machines, steel furnitures, household electric appliances, plastics, and the like, especially, coatings required to have an excellent durability.

BACKGROUND ART

Conventional thermosetting coatings are ones wherein a melamine is used as a crosslinking agent such as an alkyd melamine, an acrylic melamine or an epoxy melamine, so they are ones wherein a problem as to a bad-smelling caused by the melamine resins remains to be solved.

As coatings having no such a problem, there has been proposed (1) a paint using a polyol resin and a hydrolyzable silyl group-containing resin, (2) a paint using a polyol resin and a hydrolyzable silicon compound, (3) a paint using a hydrolyzable silyl group-containing resin and a hydrolyzable silicon compound, and the like, and it has been shown that they are additionally improved in coating film hardness, solvent resistance of the coating film, and the like.

These paints having no problem as to the bad-smelling caused by the melamines have, however, another problem that the film properties are not necessarily sufficient.

In view of the circumstances, in order to obtain coating materials having no problem as to the bad-smelling and having excellent coating film properties, the present inventors have repeated earnest studies. As a result, they have found that coating film properties can be improved by further adding a hydrolyzable silicon compound to a mixture of a resin having hydroxyl group and a hydrolyzable silyl group-containing polymer, and have accomplished the present invention.

DISCLOSURE OF THE INVENTION

The present invention relates to a thermosetting composition comprising:

- (A) a resin having a hydroxyl group,
- (B) a hydrolyzable silyl group-containing polymer,
- (C) a hydrolyzable silicon compound and
- (D) a curing catalyst.

As the resin having hydroxyl group used in the present invention which is the component (A) (hereinafter referred to as "resin (A) having hydroxyl group"), there are exemplified an alkyd resin having an oil length of not more than 50 % or oil free alkyd resin, an acrylic modified alkyd resin, a hydroxyl group-containing acrylic resin, an epoxy resin, a hydroxyl group-containing fluorocarbon resin, which have hitherto been used as the thermosetting paint, a polyester-polyol, a polyether-polyol, a polyurethane-polyol, a hydroxy group-containing cellulose compound, and the like, and the resins are not limited thereto. Such resins (A) having hydroxyl group can be prepared in a manner which has hitherto been known.

The molecular weight and the hydroxyl value of the resin (A) having hydroxyl group are not particularly limited, and resins usually used can be used. It is preferable that the number average molecular weight is from 1,500 to 40,000 from the viewpoints of the physical properties of the coating film obtained from the composition of the present invention. Also, it is preferable that the hydroxyl value is from 10 to 150 mgKOH/g from the viewpoints of the coating film physical properties. The resin (A) having hydroxyl group may be used alone or as an admixture thereof.

The hydrolyzable silyl group-containing polymer used in the present invention which is the component (B) (hereinafter referred to as "hydrolyzable silyl group-containing polymer (B)") is a silyl group-containing polymer having at the molecular ends or side chains at least one, preferably not less than two silicon atoms to which a hydrolyzable group is attached in one molecule. When the number of the hydrolyzable silyl group is less than one in one molecule, it is easy to lower the solvent resistance which is the physical property of the coating film of the composition of the present invention. Examples of the above-mentioned hydrolyzable groups are, for instance, an alkoxy group, a hydroxy group, an acyloxy group, an aminoxy group, a phenoxy group, a thioalkoxy group, an amino group, and the like. The alkoxy group is the most preferable from the viewpoint of the coating film physical properties of the composition of the present

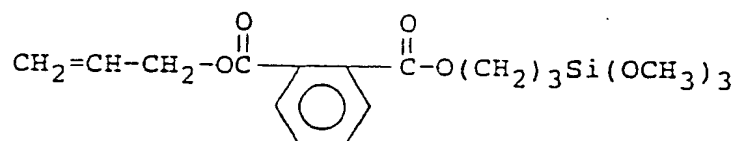
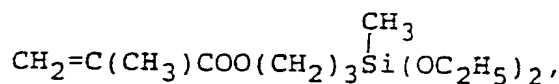
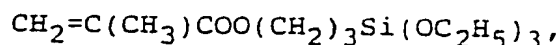
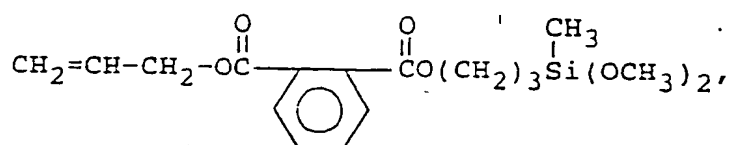
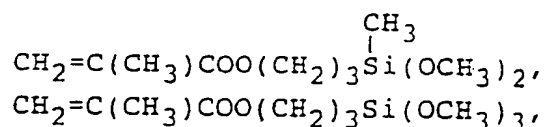
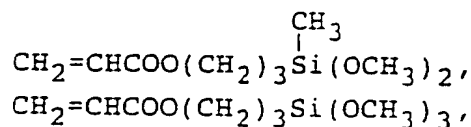
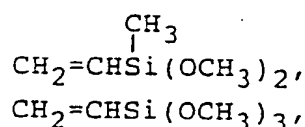
invention. It is preferable that the number average molecular weight of the hydrolyzable silyl group-containing polymer (B) is from 1,000 to 30,000 from the viewpoints of the coating film physical properties of the composition of the invention.

Concrete examples of the hydrolyzable silyl group-containing polymer (B) are a hydrolyzable silyl group-containing vinyl polymer whose main chain is substantially composed of polyvinyl bondings, a hydrolyzable silyl group-containing polyester polymer whose main chain is substantially composed of polyester bondings, a hydrolyzable silyl group-containing polyether polymer whose main chain is substantially composed of polyether bondings, furthermore, graft polymers or block polymers obtained by using them, and the polymers are not limited thereto. Among them, the hydrolyzable silyl group-containing vinyl polymers are particularly preferable from the viewpoint of the weatherability.

The above-mentioned hydrolyzable silyl group-containing vinyl polymers can be obtained by, for instance, the copolymerization of a vinyl monomer with a hydrolyzable silyl group-containing monomer. The polymer may have a urethane bond or a siloxane bond in its main chain or side chains in part.

The above-mentioned vinyl monomers are not particularly limited. Examples of the vinyl monomers are, for instance, an unsaturated carboxylic acid ester such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, stearyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, trifluoroethyl (meth)acrylate, pentafluoropropyl (meth)acrylate, a diester or half ester of a polycarboxylic acid (maleic acid, fumaric acid, itaconic acid, and the like) with a linear or branched alcohol having 1 to 20 carbon atoms; an aromatic hydrocarbon vinyl compound such as styrene, α -methylstyrene, chlorostyrene, styrenesulfonic acid, 4-hydroxystyrene or vinyl toluene; a vinyl ester or an allyl compound such as vinyl acetate, vinyl propionate or diallyl phthalate; a nitrile group-containing vinyl compound such as (meth)acrylonitrile; an epoxy group-containing vinyl compound such as glycidyl (meth)acrylate; an amino group-containing vinyl compound such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, vinylpyridine, aminoethyl vinyl ether; an amido group-containing vinyl compound such as (meth)acrylamide, itaconic diamide, α -ethyl (meth)acrylamide, crotonamide, malediamide, fumardiamide, N-vinyl pyrrolidone, N-butoxymethyl (meth)acrylamide, N,N-dimethylacrylamide, N-methylacrylamide or acryloyl morpholine; a hydroxy group-containing vinyl compound such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxyethyl vinyl ether, N-methylol(meth)acrylamide, or Aronix 5700 made by Toagosei Chemical Industry Co., Ltd., Placel FA-1, Placel FA-4, Placel FM-1 or Placel FM-4 made by Daicel Chemical Industries, Ltd.; an unsaturated carboxylic acid such as (meth)acrylic acid, maleic acid, fumaric acid or itaconic acid, their salts (an alkali metal salt, an ammonium salt, an amine salt, and the like) or their acid anhydrides (maleic anhydride); an other vinyl compound such as vinyl methyl ether, vinyl chloride, vinylidene chloride, chloroprene, propylene, butadiene, isoprene, maleimide, N-vinylimidazole or vinylsulfonic acid; and the like.

The above-mentioned hydrolyzable silyl group-containing monomers are not particularly limited so long as the monomer has the hydrolyzable silyl group. Typical examples of the monomers are, for instance,



A percentage of the hydrolyzable silyl group-containing monomer units in the hydrolyzable silyl group-containing vinyl polymer (B) is preferably from 5 to 90 % (% by weight, hereinafter the same), more preferably from 11 to 70 %.

The hydrolyzable silyl group-containing vinyl polymer can be prepared, for instance, in a manner as described in Japanese Unexamined Patent Publications No. 36395/1979, No. 36109/1982, No. 157810/1983, and the like. It is the most preferable to prepare in a solution polymerization using an azo radical initiator such as azobisisobutyronitrile from the viewpoint of the easiness of synthesis.

If necessary, in the above-mentioned solution polymerization, the molecular weight can be controlled by using a chain transfer agent such as n-dodecyl mercaptan, t-dodecyl mercaptan, n-butyl mercaptan, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropylmethyldiethoxysilane, $(\text{CH}_3)_3\text{Si}-\text{S}-\text{S}-\text{Si}(\text{OCH}_3)_3$ or $(\text{CH}_3\text{O})_3\text{Si}-\text{S}_8-\text{Si}(\text{OCH}_3)_3$. Particularly, when using a chain transfer agent having a hydrolyzable silyl group in its molecule, such as γ -mercaptopropyltrimethoxysilane, it is possible to introduce the hydrolyzable silyl group into the polymer ends of the silyl group-containing vinyl copolymer.

Polymerization solvents used in the above-mentioned solution polymerization are not particularly limited so long as the solvents are non-reactive solvents such as hydrocarbons (toluene, xylene, n-hexane, cyclohexane and the like), acetic esters (ethyl acetate, butyl acetate and the like), alcohols (methanol, ethanol, isopropanol, n-butanol and the like), ethers (ethyl cellosolve, butyl cellosolve, cellosolve acetate and the like), and ketones (methyl ethyl ketone, ethyl acetoacetate, acetylacetone, diacetone alcohol, methyl isobutyl ketone, acetone and the like).

The hydrolyzable silyl group-containing polymer (B) may be used alone or as an admixture thereof.

The used amount of the hydrolyzable silyl group-containing polymer (B) is not particularly limited. It is preferable that the component (A) / the compound (B) is from 9/1 to 1/9 in weight ratio, more preferably from 8/2 to 2/8. When (A)/(B) is more than 9/1, it tends to lower the water resistance, the coating film physical property of the composition of the present invention, and when (A)/(B) is less than 1/9, there is a tendency that the characteristics obtained by blending the component (A) are unsatisfactorily obtained.

The hydrolyzable silicon compound used in the present invention which is the component (C) (hereinafter referred to as "hydrolyzable silicon compound (C)") is a compound having a hydrolyzable silyl group at the molecular end or side chain, and is a component used for improving adhesion, hardness and solvent resistance of coating films obtained from the thermosetting composition comprising the resin (A) having hydroxyl group, the hydrolyzable silyl group-containing polymer (B) and the curing catalyst (D) mentioned below.

Preferable examples of the hydrolyzable silicon compound (C) are, for instance, hydrolyzable silane compounds, their condensation products, their reaction products, mixtures thereof, and the like.

Concrete examples of the above-mentioned hydrolyzable silane compounds are, for instance, methyl silicate, methyltrimethoxysilane, ethyltrimethoxysilane, butyltrimethoxysilane, octyltrimethoxysilane, dodecyltrimethoxysilane, phenyltrimethoxysilane, vinyltrimethoxysilane, γ -methacryloyloxypropyltrimethoxysilane, γ -acryloyloxypropyltrimethoxysilane, γ -glycidoxypyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -aminopropyltrimethoxysilane, N- β -aminoethyl- γ -propyltrimethoxysilane, dimethyldimethoxysilane, diethyldimethoxysilane, dibutyldimethoxysilane, diphenyldimethoxysilane, vinylmethyldimethoxysilane, γ -methacryloyloxypropylmethyldimethoxysilane, trimethylmethoxysilane, triethylmethoxysilane, triphenylmethoxysilane, ethyl silicate, methyltriethoxysilane, ethyltriethoxysilane, butyltriethoxysilane, octyltriethoxysilane, dodecyltriethoxysilane, phenyltriethoxysilane, vinyltriethoxysilane, γ -methacryloyloxypropyltriethoxysilane, γ -acryloyloxypropyltriethoxysilane, γ -glycidoxypyltriethoxysilane, γ -mercaptopropyltriethoxysilane, γ -aminopropyltriethoxysilane, N- β -aminoethyl- γ -propyltriethoxysilane, dimethyldiethoxysilane, diethyldiethoxysilane, dibutyldiethoxysilane, diphenyldiethoxysilane, vinylmethyldiethoxysilane, γ -methacryloyloxypropylmethyldiethoxysilane, trimethylethoxysilane, triethylethoxysilane, triphenylmethoxysilane, and the like.

Also, the partially hydrolyzed condensate of the above-mentioned hydrolyzable silane compound can be easily obtained by progress of the condensation of the above-mentioned silane compound or the admixture thereof, adding a necessary amount of H₂O, also adding, as occasion demands, a small amount of a condensation catalyst such as hydrochloric acid or sulfuric acid at a temperature of ordinary temperature to 100 °C while removing a generated alcohol.

As a partially hydrolyzed condensate of methyl silicate which has methoxysilyl group, there are exemplified, for instance, Methyl Silicate 47, Methyl Silicate 51, Methyl Silicate 55, Methyl Silicate 58, Methyl Silicate 60, which are made by NIPPON COLCOAT Kabushiki Kaisha, and the like. Also, as a partially hydrolyzed condensate of methyltrimethoxysilane or dimethyldimethoxysilane which has methoxysilyl group, there are exemplified AFP-1, AFP-2, AFP-6, KR213, KR217, KR9218, which are made by Shin-Etsu Chemical Co., Ltd.; TSR165, TR3357, which are made by Toshiba Silicone Co., Ltd., Y-1587, FZ-3701, FZ-3704, which are made by Nippon Unicar Kabushiki Kaisha and the like. Also, as a partially hydrolyzed condensate of ethyl silicate which has ethoxysilyl group, there are exemplified Ethyl Silicate 40 which is made by NIPPON COLCOAT Kabushiki Kaisha, HAS-1, HAS-6, HAS-10, and the like.

As the reaction product of the above-mentioned hydrolyzable silane compound, there are exemplified, for instance, reaction products of a silane coupling agent having amino group and a silane coupling agent having epoxy group; reaction products of a silane coupling agent having amino group and ethylene oxide, butylene oxide, epichlorohydrin, epoxidated soybean oil, an other compound having epoxy group such as Epicoat 828 or Epicoat 1001, made by Yuka Shell Epoxy Kabushiki Kaisha; reaction products of a silane coupling agent having epoxy group and an amine, for instance, an aliphatic amine such as ethyl amine, diethyl amine, triethyl amine, ethylene diamine, hexane diamine, diethylene triamine, triethylene tetramine or tetraethylene pentamine, an aromatic amine such as aniline or diphenyl amine, an alicyclic amine such as cyclopentyl amine or cyclohexyl amine, ethanol amines; and the like.

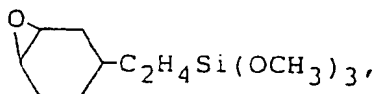
The hydrolyzable silicon compound (C) may be used alone or as an admixture thereof.

The used amount of the hydrolyzable silicon compound (C) is not particularly limited. Generally the amount is from 0.01 to 100 parts (part by weight, hereinafter the same), preferably from 0.1 to 30 parts, based on 100 parts of the solid matter of the component (A) and the component (B). When the used amount of the component (C) is less than 0.01 part, the addition effect can be unsufficiently obtained. When the amount is more than 100 parts, it tends to lower the coating film properties of the composition of the present invention.

Examples of the curing catalyst used in the present invention which is the component (D) (hereinafter referred to as "curing catalyst (D)") are, for instance, organotin compounds such as dibutyl tin dilaurate,

dibutyl tin dimaleate, dioctyl tin dilaurate, dioctyl tin dimaleate and tin octoate; phosphoric acid or phosphates such as monomethyl phosphate, monoethyl phosphate, monobutyl phosphate, monoctyl phosphate, monodecyl phosphate, dimethyl phosphate, diethyl phosphate, dibutyl phosphate, dioctyl phosphate and didecyl phosphate; addition reaction products of phosphoric acid and (or) mono-acid phosphate with an epoxy compound such as propylene oxide, butylene oxide, cyclohexene oxide, glycidyl methacrylate, glycidol, acryl glycidyl ether, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldimethoxysilane,

10



Cardula E made by Yuka Schell Epoxy Kabushiki Kaisha, or Epicote 828 or Epicote 1001 made by Yuka Shell Epoxy Kabushiki Kaisha; organic titanate compounds; organic aluminum compounds; acidic compounds such as maleic acid and p-toluenesulfonic acid; amines such as hexylamine, di-2-ethylhexylamine, N,N-dimethyldodecylamine and dodecylamine; reaction products of the amine with the acidic phosphate, alkaline compounds such as sodium hydroxide and potassium hydroxide; and the like.

Among these curing catalysts (D), the organotin compounds, the acidic phosphate, the reaction products of the acidic phosphate and the amine, the saturated or unsaturated polyvalent carboxylic acids or their acid anhydrides, the reactive silicon compounds, the organic titanate compounds, the organic aluminum compounds, and mixtures thereof have high activity, and are preferable.

The curing catalyst (D) may be used alone or as an admixture thereof.

The used amount of the component (D) is not particularly limited. The amount is usually from 0.1 to 20 parts, preferably from 0.1 to 10 parts, based on 100 parts of the solid matter of the component (A) and the component (B). When the used amount of the component (D) is less than 0.1 part, the curability tends to lower. When the amount is more than 20 parts, the coating film properties of the composition of the present invention tend to lower.

When as the component (D), the reactive silicon compound which is also used as the component (C) is used, it is preferable that the used amount is not more than 30 parts [total amount of the component (C) and the component (D)] based on the solid matter of the component (A) and the component (B).

In the composition of the present invention, a dehydrating agent may be used or not. By using the dehydrating agent, the stability maintained for a long period of time and the stability such that even if the composition is used repeatedly, no problem arises can be obtained.

Examples of the dehydrating agents are, for instance, hydrolyzable ester compounds such as methyl orthoformate, ethyl orthoformate, methyl orthoacetate, ethyl orthoacetate, methyltrimethoxysilane, γ -methacryloyloxypropyltrimethoxysilane, vinyltrimethoxysilane, methyl silicate and ethyl silicate, and the like. These dehydrating agents may be added before, after or during the polymerization of the hydrolyzable silyl group-containing polymer (B).

The used amount of the dehydrating agent is not particularly limited. The amount is usually not more than 100 parts, preferably not more than 50 parts, based on 100 parts of the solid matter of the component (A) and the component (B).

Further, it is possible to increase the effect of the dehydrating agent by the combination with a dehydrating accelerator.

As the dehydrating accelerator, there are effective inorganic acid such as hydrochloric acid, sulfuric acid, phosphoric acid or nitric acid; an organic acid such as formic acid, acetic acid, oxalic acid, benzoic acid, phthalic acid, p-toluenesulfonic acid, acrylic acid and methacrylic acid; a metal salt of carboxylic acid such as an alkyl titanate or lead octylate; a carboxylic acid organotin compound such as tin octylate, dibutyl tin dilaurate or dioctyl tin maleate; a sulfide or mercaptide organotin compound such as monobutyl tin sulfide or dioctyl tin mercaptide; an organotin oxide such as dioctyl tin oxide; an organotin compound obtained by the reaction of the organotin oxide and an ester compound such as ethyl silicate, Ethyl Silicate 40, dimethyl maleate or dioctyl phthalate; an amine such as tetraethylenepentamine, triethylenediamine or N- β -aminoethyl- γ -aminopropyltrimethoxysilane; an alkali catalyst such as potassium hydroxide or sodium hydroxide; and the like. Among them, the organic acids, the inorganic acids and the organotin compounds are particularly effective.

The dehydrating accelerator is used in an amount from 0.0001 to 20 parts, preferably from 0.001 to 10 parts, based on 100 parts of the dehydrating agent. When using the compound which is also used as the above-mentioned component (D) as the dehydrating accelerator, it is further used in amount of 0.1 to 20

parts, preferably from 0.1 to 10 parts, in addition to the used amount of the above-mentioned component (D).

In the composition of the present invention, a solvent may be used. As the solvent to be used, any of solvents such that both the resin (A) having hydroxyl group and the hydrolyzable silyl group-containing polymer (B) are dissolved therein or any of solvents such that no precipitate is produced when mixing the resin (A) having hydroxyl group with the hydrolyzable silyl group-containing polymer (B) are used.

Concrete examples of such solvents are, for instance, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ketones, esters, ethers, alcoholic esters, ketone alcohols, ether alcohols, ketone ethers, ketone esters, ester ethers, which are used in usual paints or coating agents, and the like. Among them, solvents containing alkyl alcohols are particularly preferable from the viewpoint of the increase of the stability of the composition of the invention.

As the above-mentioned alkyl alcohol, alkyl alcohols having an alkyl group with 1 to 10 carbon atoms are preferable. For instance, there is used methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, n-amyl alcohol, isoamyl alcohol, hexyl alcohol, octyl alcohol, cellosolve, or the like. The used amount of the alcohol is not particularly limited. Usually, the amount is not more than 100 parts, preferably not more than 50 parts, based on 100 parts of the solid matter of the component (A) and the component (B).

The combination of the alcohol and the above-mentioned dehydrating agent is remarkably effective to the storage stability in case of mixing the components (A), (B) and (C) of the composition of the present invention and storing it. The amount of the solvent varies depending on the molecular weight or the composition of the components (A) and (B) used in the composition of the present invention, and it is adjusted to a practically necessary solid content or viscosity.

To the composition of the present invention may be added, according to the uses thereof, additives such as diluents, pigments (including an extender pigment), ultraviolet absorbers, light stabilizers, agents for preventing precipitation and leveling agents; celluloses such as nitrocellulose and cellulose acetate butyrate, resins such as epoxy resins, melamine resins, vinyl chloride resins, chlorinated polypropylene, chlorinated rubbers and polyvinyl butyral, fillers, and the like.

Next, the preparation method of the composition of the present invention is explained.

The preparation method is not particularly limited. For instance, the composition of the present invention is prepared in a manner wherein the component (A) is cold-blended with the component (B), or after mixing the components (A) and (B) it is heated (hot-blended) to partially react, to which the components (C) and (D) are added.

Thus obtained composition of the present invention is one wherein the crosslinking reaction that hydroxyl group of the resin (A) having hydroxyl group reacts with silyl group of the hydrolyzable silyl group-containing polymer (B) is utilized, and it is clearly distinguished from conventional techniques using a melamine as the crosslinking agent.

The composition of the present invention can be cured at a temperature of usually not less than 30 °C, preferably from 55 °C to 350 °C, after applying it to a substrate according to a usual manner such as dipping manner, spraying or brushing.

The coating films obtained from the composition of the present invention are excellent in adhesion, solvent resistance, hardness, and the like and have high durability.

BEST MODE FOR CARRYING OUT THE INVENTION

The composition of the present invention is explained by means of Preparation Examples, Examples and Comparative Examples.

Preparation Example 1

[Preparation of a hydrolyzable silyl group-containing polymer (B)]

A reactor equipped with a stirrer, a thermometer, a condenser, a nitrogen inlet tube and a dropping funnel was charged with 45.9 parts of xylene, and the reactor was heated to 110 °C, introducing nitrogen gas thereto. Then, a mixture (b) as shown below was added dropwise at a uniform velocity through the dropping funnel for 5 hours.

Mixture (b)

Styrene	12.8 parts
Methyl methacrylate	50.1 parts
Stearyl methacrylate	6.9 parts
γ -Methacryloyloxypropyltrimethoxysilane	30.2 parts
Xylene	13.5 parts
2,2'-Azobisisobutyronitrile	4.5 parts

After completing the addition of the mixture (b), 0.5 part of 2,2'-azobisisobutyronitrile and 5 parts of toluene were added dropwise at a uniform velocity for 1 hour. After completing the addition, the resulting mixture was aged at 110°C for 2 hours, then was cooled down and xylene was added to the resin solution to adjust the solid content to 60 %. The properties of the obtained resin solution (1) are shown in Table 1.

Preparation Example 2

[Preparation of resin (A) having hydroxyl group]

The reactor was charged with 31.3 parts of butyl acetate and 9.5 parts of xylene instead of 45.9 parts of xylene, and a mixture (a) as shown below was added in the same manner as in Preparation Example 1.

Mixture (a)

Xylene	18 parts
Styrene	28.3 parts
Methyl methacrylate	7.1 parts
n-Butyl acrylate	32.5 parts
Methacrylic acid	0.3 parts
Placel FM-1 (Note 1)	31.8 parts
2,2'-Azobisisobutyronitrile	1.8 parts
(Note 1) 2-Hydroxyethyl methacrylate/ ϵ -caprolactone	
= 1/1 addition reaction product made by Daicel Chemical Industry Co., Ltd.	

After completing the addition of the mixture (a), 0.2 part of 2,2'-azobisisobutyronitrile and 3.8 parts of toluene were added dropwise at a uniform velocity for 1 hour. After completing the addition, the resulting mixture was aged at 110°C for 2 hours, then the mixture was cooled down. Xylene was added to the resin solution to adjust the solid content to 60 %. The properties of the resin solution (2) are shown in Table 1.

Table 1

Resin solution	(1)	(2)
Physical Property		
Non-volatile matter (%)	60	60
Viscosity (28°C, cps)	900	4,400
Acid value (mgKOH/g solid)	0	2.0
Hydroxyl value (mgKOH/g solid)	0	73
Number average molecular weight	6,000	10,000
Color number (Gardner)	<1	<1

Examples 1-3 and Comparative Example 1

To 48g of the resin solution (1) was added 72 g of the resin solution (2), 48 g of titanium dioxide (CR 93 made by Ishihara Industry Kabushiki Kaisha), 3.6 g of methyl orthoacetate, 10 g of isopropyl alcohol, 18.4 g of xylene, and 80 g of glass beads having a particle size of 2 mm ϕ , and the mixture was dispersed by a paint shaker for 1 hour to give a white enamel-1.

The obtained white enamel-1, a hydrolyzable silicon compound and dibutyl tin dilaurate were mixed in amounts as shown in Table 2 to prepare a composition.

To the obtained composition was added a mixed solvent of xylene/butanol = 70 / 30 to dilute to a coating viscosity, with which a test piece [an anti-corrosive aluminum (A-5052P made by Nippon Test Panel Kabushiki Kaisha) was degreased with xylene] was air-sprayed, and it was allowed to stand for 20 minutes and was baked at 140°C for 20 minutes to give a film with a thickness of 30 μ m. The pencil hardness, the state after 10 times xylene rubbing and the adhesion of the obtained coating film were estimated according to the following methods. The results are shown in Table 2.

(Pencil hardness)

A test and estimation are conducted according to JIS K 5400.

(State after 10 times xylene-rubbing)

An absorbent cotton is impregnated with xylene, with which each test piece is rubbed 10 times under the same condition, and the state is observed. Estimations are that \odot shows no damage, \bigcirc shows a state that a few scratches are observed on the surface, Δ shows a state that the gloss a little wears out and x shows a state that there is no gloss. [Adhesion]

According to a cross-cut test method in the manner described in JIS K 5400, the estimations are conducted as 10 shows 100/100 and 0 shows 0/100.

Comparative Example 2

To 120 g of the resin solution (2) obtained in Preparation Example 2 [resin (A) having hydroxyl group] was added 48 g of titanium dioxide (CR 93 made by Ishihara Industry Kabushiki Kaisha), 3.6 g of methyl orthoacetate, 10 g of isobutyl alcohol, 13.4 g of xylene, and 80 g of glass beads having a particle size of 2 mm ϕ , and the mixture was dispersed by a paint shaker for 1 hour to give a white enamel-2.

The obtained white enamel-2, a hydrolyzable silicon compound and dibutyl tin dilaurate were mixed in amounts as shown in Table 2 to prepare a composition.

In the same manner as in Example 1, the obtained composition was diluted, the test piece was air-sprayed to give a coating film and the estimations were conducted. The results are shown in Table 2.

Comparative Example 3

To 120 g of the resin solution (1) obtained in Preparation Example 1 [hydrolyzable silyl group-containing polymer (B)] was added 48 g of titanium dioxide (CR 93 made by Ishihara Industry Kabushiki Kaisha), 3.6 g of methyl orthoacetate, 10 g of isobutyl alcohol, 13.4 g of xylene, and 80 g of glass beads having a particle size of 2 mm ϕ , and the mixture was dispersed by a paint shaker for 1 hour to give a white enamel-3.

The obtained white enamel-3, a hydrolyzable silicon compound and dibutyl tin dilaurate were mixed in amounts as shown in Table 2 to prepare a composition.

In the same manner as in Example 1, the composition was diluted, the test piece was air-sprayed to give a coating film and the estimations were conducted. The results are shown in Table 2.

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Table 2

Ex. No.	1	2	3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Composition (part)						
White enamel 1	100	100	100	100	-	-
" 2	-	-	-	-	100	-
" 3	-	-	-	-	-	100
Hydrolyzable						
silicon compound 1*1	0.72	-	0.36	-	-	-
" 2*2	-	1.8	-	-	-	-
" 3*3	-	-	1.8	-	1.8	1.8
Dibutyl tin dilaurate	1.4	1.4	1.4	1.4	1.4	1.4

- continued -

- continued -

Ex. No.	1	2	3	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3
Estimation results						
Pencil hardness	H	H	2H	F	2B	B-HB
10 times Xylene-rubbing	⊙	⊙	⊙	○	X	△
Adhesion (marks)	10	10	10	7	10	9

*1 A reaction product of an aminosilane (A-1120 made by Union Carbide Coporation) and an epoxysilane (A187 made by Union Carbide Coporation)

*2 A reaction product of an epoxy resin (Epicoat 828 made by Yuka Shell Epoxy Kabushiki Kaisha) and an aminosilane (A-1100 made by Union Carbide Coporation)

*3 A hydrolyzed condensate of ethyl silicate (Ethyl Silicate made by NIPPON COLCOAT Kabushiki Kaisha)

From the results of Table 2, it would be understood that the coating films using the coating materials relating to the composition of the present invention wherein the hydrolyzable silicon compound is added are improved in pencil hardness, solvent resistance shown by the state after 10 times xylene rubbing, and adhesion.

INDUSTRIAL APPLICABILITY

When using the thermosetting composition of the present invention, the coating materials having no problem as to the bad-smelling can be obtained and the coating films having improved properties such as adhesion, solvent resistance and hardness can be obtained.

Claims

1. A thermosetting composition comprising:
 - (A) a resin having hydroxyl group,
 - (B) a hydrolyzable silyl group-containing polymer,
 - (C) a hydrolyzable silicon compound and
 - (D) a curing catalyst
2. The thermosetting composition of Claim 1, wherein said resin having hydroxyl group which is the component (A) has a hydroxyl value of 10 to 150 mg KOH/g and a number average molecular weight of 1,500 to 40,000.
3. The thermosetting composition of Claim 1 wherein said hydrolyzable silyl group-containing polymer which is the component (B) is a polymer having 5 to 90 % by weight of units derived from an alkoxysilyl vinyl monomer having a polymerizable unsaturated double bond and an alkoxysilyl group in its molecule.
4. The thermosetting composition of Claim 1, wherein said hydrolyzable silicon compound which is the component (C) is a hydrolyzable silane compound, its condensation product, its reaction product or a mixture thereof.
5. The thermosetting composition of Claim 1, wherein said curing catalyst which is the component (D) is an organotin compound, an acidic phosphate, a reaction product of an acidic phosphate with an amine, a saturated or unsaturated polyvalent carboxylic acid, a saturated or unsaturated polyvalent carboxylic acid anhydride, a reactive silicon compound, an organic titanate compound, an organic aluminum compound or a mixture thereof.
6. The thermosetting composition of Claim 1, which further have a hydrolyzable ester compound as a dehydrating agent and an alkyl alcohol as a solvent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00152

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁵ C08L101/10		
II. FIELDS SEARCHED		
Classification System :		Minimum Documentation Searched :
IPC		Classification Symbols
C08L101/00 - 101/10		
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁶		
Jitsuyo Shinan Koho		1947 - 1989
Kokai Jitsuyo Shinan Koho		1973 - 1989
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁷		
Category ⁸	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	JP, A, 58-225155 (Dainippon Ink and Chemicals, Inc.), 27 December 1983 (27. 12. 83), (Family: none)	1 - 6
X	JP, A, 58-171446 (Dainippon Ink and Chemicals, Inc.), 8 October 1983 (08. 10. 83), (Family: none)	1 - 6
X	JP, A, 58-111855 (Kanegafuchi Chemical Industry Co., Ltd.), 4 July 1983 (04. 07. 83), (Family: none)	1 - 6
<p>¹⁴ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
April 20, 1990 (20. 04. 90)		May 7, 1990 (07. 05. 90)
International Searching Authority		Signature of Authorized Officer
Japanese Patent Office		

Form PCT ISA 210 (second sheet) (January 1985)

Patent Abstracts of Japan

cited in the European Search
Report of EP 00355003.6
Your Ref.: F-P02012 TB(EP)

PUBLICATION NUMBER : 61101527
PUBLICATION DATE : 20-05-86

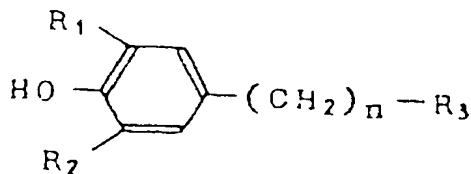
APPLICATION DATE : 24-10-84
APPLICATION NUMBER : 59221982

APPLICANT : TORAY IND INC;

INVENTOR : OKASAKA HIDESADA;

INT.CL. : C08G 63/22

TITLE : PRODUCTION OF POLYESTER



ABSTRACT : PURPOSE: To produce a polyester which can form a film excellent in transparency, flatness, slidability and electrical properties, by adding a phosphorous compound and a specified amount of fine particles to the reaction mixture during polycondensation reaction.

CONSTITUTION: In the production of a polyester consisting mainly of repeating units of ethylene terephthalate, 0.05~5wt% phosphorus compound of a MW ≥ 300 and 0.005~2wt% fine particles of an average particle diameter of 0.03~3 μ m are added to the reaction mixture during the reaction from the time before the start of esterification or transesterification to the time of completion of polycondensation reaction. As the phosphorus compounds, those containing a phenolic hydroxyl group of the formula (wherein R_1 and R_2 are each a 1~10C alkyl, R_3 is a 2~24C phosphinate or phosphonate group and n is 0~5) are desirable. As said fine particles, those of e.g., calcium carbonate, silicon dioxide, etc., are used.

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⑨ 日本国特許庁(JP)

⑩ 特許出願公開

⑪ 公開特許公報(A)

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識別記号

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⑬ 公開 昭和61年(1986)5月20日

C 08 G 63/22

6537-4J

審査請求 未請求 発明の数 1 (全6頁)

⑭ 発明の名称 ポリエステルの製造方法

⑮ 特 願 昭59-221982

⑯ 出 願 昭59(1984)10月24日

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明 細 書

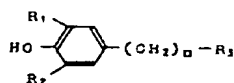
1. 発明の名称

ポリエステル¹の製造方法

2. 特許請求の範囲

(1) 主たるくりかえし単位がエチレンテレフタレートであるポリエステルを製造する際、エステル化またはエステル交換反応開始前から重合反応が終了するまでの間に分子量300以上のリン化合物0.05～5.0重量%と平均粒径0.03～3.0 μ の微細粒子を0.005～2.0重量%添加することを特徴とするポリエステルの製造方法。

(2) 上記リン化合物が下記一般式で表わされるフェノール性水酸基含有リン化合物である特許請求の範囲第(1)項記載のポリエステルの製造方法。



ここで α は0～5の整数である。

R_1 および R_2 は水素または $C=1\sim 10$ のアルキル基、 R_3 は $C=2\sim 24$ のホスフィン酸エステル基またはホスホン酸エステル基である。

3. 発明の詳細を説明

(技術分野)

本発明は特定のリン化合物と微細な粒子の各特定量を含むポリエステル、特に透明性、平坦性、滑性および電気特性に優れたフィルム形成性ポリエステルの製造方法に関するものである。

(従来技術およびその問題点)

近年ポリエチレンテレフタレート²は電気テープ用、写真用、コンデンサー用、包装用、マイクロフィルム用などの分野への進展が著しい。

従来フィルムの透明性を向上させる目的で様々な方法が提案されてきた。しかし、これらの方法はいずれも透明性に重点を置いているために得られるフィルムは著しく脆性が劣る欠点

があつた。

要求特性のうち、特に易滑性の付与は重要で表面が易滑性でないとフィルムとフィルムの間で滑現象が起こり、製膜時あるいは後加工時に作業能率が低下するばかりでなく捲き裂を惹くするため製品価値を著しく低下させるなどの問題を引き起こすことになる。

一方、磁気テープ用途などの磁気記録媒体として使用する場合に出力の低下やドロップアウトを防止するため表面凹凸の少ない、いわゆる平坦性に優れていることが必要で、かつ滑性に優れることが要求される。

また、コンデンサー用フィルム用途においても互いに相反する電気特性と滑り性を兼備せしめる要求がある。

これらの問題点を解決する目的で従来から数多くの技術が提案され実施されているが大別すると二酸化チタン、タルク、カオリナイト、炭酸カルシウム、酸化ケイ素などのポリエステル合成反応系に不活性な微粒子を添加する方法や

ポリエステル合成時に使用する触媒、着色防止剤などの一部または全部を反応の過程で析出せしめ微粒子として存在させる方法がある。

しかし、これらの方法で得たフィルムは平坦性を維持した状態で十分な滑性を得ることができないのである。

例えばコンデンサー用フィルムの電気特性と滑り性の改良を目的とした特開昭55-21157号公報が知られている。これはカルシウム化合物の存在下でポリエステルのエステル交換反応を行ないカルシウム化合物に対して1〜2倍モルのリン化合物を添加し、かつ特定の不活性粒子を添加してなるポリエステルフィルムである。しかし、このフィルムは十分な滑り性を付与するために不活性粒子を添加していくと良好な電気特性が得られにくい欠点がある。

一方、特公昭34-5144号公報では3個のリン化合物を併用する方法が開示されているが、この場合はテレフタル酸のアルカリ土類金属塩微粒子はむしろ減少してしまい得られたフィルム

は透明性、平坦性、電気特性において優れているが滑り特性不足で捲き工程においてブロッグ化してしまう問題があつた。

〔発明の目的〕

本発明の目的はこれら従来技術で達成し得なかつた透明性、平坦性、滑性および電気特性を兼備したフィルム形成性ポリエステルの製造方法に関するものである。

〔発明の構成〕

前記した本発明の目的は主たるくりかえし単位がエチレンテレフタレートであるポリエステルを製造する際、エステル化またはエステル交換反応開始前から重合反応が終了するまでの間に分子重300以上のリン化合物0.05〜5.0重量%と、平均粒径0.03〜5.0 μ mの微細粒子を0.005〜2.0重量%添加することを経験とするポリエステルの製造方法によつて達成できる。

次に本発明を詳細に説明するが本発明のポリエステルとは繊維、フィルム、その他の成形品

に成形し得るポリエチレンテレフタレートを主体とするものであつて従来公知の様々な方法によつて製造されるものである。もちろん、これらのポリエステルはホモポリエステルであつてもコポリエステルであつてもよく、共重合する成分は例えば、ジエチレングリコール、プロピレングリコール、ネオペンタグリコール、ポリアルキレングリコール、p-キシリレンジリコール、1,4-シクロヘキサジメタノール、5-ナトリウムスルホレゾルシンなどのジオール成分、アジピン酸、セバシン酸、フタル酸、イソフタル酸、2,6-ナフタリンジカルボン酸、5-ナトリウムスルホイソフタル酸などのジカルボン酸成分、トリメリット酸、ピロメリット酸などの多官能ジカルボン酸成分、p-オキシエトキシ安息香酸などのオキシカルボン酸成分などが挙げられる。

ジカルボン酸成分がジカルボン酸の場合はグリコールとのエステル化反応法、またジカルボン酸エステルの場合はグリコールとのエステル

交換反応後、高圧、減圧下にて重合せしめポリエステルを得る。

また、プレポリマー自身を出発物質として重合させることもできる。

本発明になる平均粒径 0.05 μ 以上 3.0 μ 以下の微細粒子とは従述する不活性粒子であつて種類としては合成または天然品として得られる炭酸カルシウム、湿式酸化ケイ素、乾式酸化ケイ素、ケイ酸アルミニウム、硫酸バリウム、リン酸カルシウム、タルク、二酸化チタン、酸化アルミニウム、水酸化アルミニウム、テフタル酸カルシウム、ケイ酸カルシウム、含フッ素系微粒子ポリマー、架橋ポリマーの微粉末などが挙げられる。これら微細粒子の添加量は 0.005 ~ 2.0 重量% であり、好ましくは 0.005 ~ 1.0 重量% であり、0.01 ~ 0.5 重量% が更に好ましい。粒子含有量が 0.005 重量% 未満ではフィルムとしたときフィルム-フィルム間、フィルム-金属間の摩擦係数が大きくなり、一方粒子含有量が 2.0 重量% を越えた場合には粗大粒子

の発生が多くなり、フィルムにしたときの平坦性が悪化され、また粗大粒子が絶縁破壊の発生源となるため絶縁破壊電圧特性が悪しく低下、熔融成形過程でのフィルターの目詰り、フィルム破れなどに悪影響を与える恐れがあり好ましくない。

また、フィルム表面の平坦性、透明性および電気特性をバランスさせるためには微細粒子の平均粒径は 0.03 ~ 3.0 μ とする必要がある、より好ましい粒子の平均粒径範囲は 0.1 ~ 2.0 μ である。

本発明のポリエステルのフィルムとした場合に粒子の平均径が 0.03 μ 未満の場合はフィルムの滑性が低下してくる。

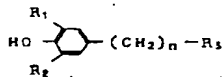
また平均径が 3.0 μ を越えると粗大粒子に起因する絶縁破壊電圧特性の低下およびフィルムの平坦性が低下してくる。

これらの微細粒子は粗大粒子の除去および粒度調整を目的に通常、用いられる種々の方法、たとえば、風分級、エタレングリコールスラ

リーまたは水スラリーとして自然沈降分離、遠心沈降分離、サントミ^{などの}粉砕および/または分級処理を採用してもよい。

本発明の分子量 300 以上、好ましくは 400 以上のリン化合物の具体例としては sec-ブタジントリフェニルフォスホラン、ベンジリデントリフェニルフォスホラン、フェニルジイソオクチルホスファイト、ジイソデシルペンタエリスリトールジフォスファイト、トリシクロヘキシルホスフェート、トリ n-ブチルフォスフェートなどが挙げられる。

これらのうちで分子量 400 以上の下記一般式に示すフェノール性水酸基含有リン化合物は最も良好な易滑性と絶縁破壊電圧などの電気特性を大巾に向上させる点で特に好ましい。



コは 0 ~ 5 の整数である。

R₁ および R₂ は水素または C = 1 ~ 10 のアルキル基、R₃ は C = 2 ~ 2.4 のホスフィン酸エステル基、ホスホン酸エステル基である。

これらリン化合物の分子量が 300 未満の場合や添加量が 0.05 重量% より少ないとポリエステルフィルムとした場合に滑性および絶縁破壊電圧などの電気特性に対する効果が得られなくなり、また 5.0 重量% より多い場合は重合生産性が悪くなり好ましくない。このためリン化合物の添加量はポリエステルに対し 0.05 ~ 5.0 重量% が望ましく、特に 0.05 ~ 3.0 重量% が好ましい。

本発明のポリエステルはそのまま用いてもよいがマスターポリマーとして用いることもできる。ポリエステルフィルムとした場合に上述したような特性を得るためにはポリエステルフィルム中のリン元素として 0.005 ~ 0.1 重量% 含有することが望ましい。そのため適宜、フィルム

中のリン元素含有量が上述した範囲になるよう希釈して使用することもできる。フィルム中のリン元素が0.1重量%を超える場合は製膜速度の低下の原因となり好ましくない。

微細粒子およびリン化合物の添加時期はポリエステル重合反応前、重合反応中、重合反応終了後の何れでもよいが、微細粒子は水および／またはエチレングリコールに分散させたスラリーとして重合反応前または反応中に添加するのが好ましい。

(発明の効果)

本発明になるポリエステルを用いて製造したフィルムの特徴は特定粒子径を有する特定量の微細粒子と特定分子量を有する特定量のリン化合物を含有するため次のような優れた効果が認められる。

- (1) フィルムの溶融成形過程でフィルターの目詰りが少なく、かつ粗大粒子によるフィルムの裂破れが少ない。
- (2) フィルム表面の平滑性に優れるため、特に

法に従って測定した。

(フィルム膜厚粗さ)

フィルム表面を触針式粗さ計によりJIS-B0601に定める方法に従い観測し、最大粗さ、平均粗さ(μ)を求めた。

(絶縁破壊電圧)

交流耐圧試験器を用い、JIS-C-2518に従って測定した。

実施例1

ジメチルテレフタレート100重量部、エチレングリコール65重量部およびエステル交換触媒として酢酸カルシウム0.09重量部、重合触媒として三酸化アンチモン0.03重量部を加え、140～220℃の間ではばらばら量のメタノールを留出させエステル交換反応を終了させた。続いて系内にトリメチルホスフェート0.04重量部と平均粒径0.3 μ の乾式シリカ(SiO_2) (日本アエロジル(株)製「アエロジル」R-972) 0.3重量部をエチレングリコールスラリーとして添加した。続いて系内を真空に減圧とし、

真空チープ用途では発生時のドロップアウト、音飛びなどの欠点がなく、極めて有用である。

- (3) 良好な耐湿性を有するため工程通過性、取扱い性に優れる。
- (4) 絶縁破壊電圧などの電気特性に優れる。

以上のように本発明のポリエステル組成物は未延伸フィルムおよび延伸フィルムとして好ましく用いることができる。

以下に実施例をあげて本発明を詳述する。

なお、実施例中のポリエステルの各特性値の測定法は次のような方法で行なった。

(粒子の粒径)

平均粒子径は粒子の光子顕微鏡または電子顕微鏡写真によつて測定した50重量%の点にあたる粒子の等価球直径により求めた。等価球直径とは粒子と同じ容積を有する球の直径である。

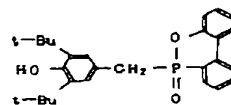
(フィルムヘイズ)

ASTM-D-1003-52に従って測定した。

(伸び係数)

スリップテスターを用い、ASTM-D-1894B

0.1mm以下の減圧下で285℃の温度にしてエチレングリコールを留去し、4時間で反応を終了した。反応終了後下記構造を有するフェノール性水酸基含有リン化合物(以後PIRと略す) 1.0重量部を添加し、約10分間の減圧留置を行ない、固有粘度0.612で SiO_2 0.3重量部を含有しているポリマーを得た。



かくして得られたポリエステルの減圧乾燥後(170℃×2時間)285℃で溶融押出し60℃の冷却ドラム上にキャストし、延伸シートとしたのも常法により長手方向3.3倍、横方向3.5倍延伸し、やや加熱しつつ215℃で焼結処理し、厚み5 μ のポリエチレンテレフタレート2 μ 延伸フィルムを得た。得られたフィルムのヘイズは1.9%で伸縮係数0.60、フィルム表面の平均粗さ0.020 μ 、フィルム表面

大粗さ0.20 μ 、絶縁破壊電圧548V/ μ と透明性、平担性、滑性、電気特性共に極めて優れていた。

実施例2

ジメチルテレフタレート100重量多、エナレングリコール65重量多およびエステル交換触媒として酢酸カルシウム0.09重量多、重合触媒として三酸化アンチモン0.03重量多を加え、140~220℃の間ではほぼ理論量のメタノールを留出させエステル交換反応を終了させた。既いて系内にトリメチルホスファート0.04重量多と平均粒径0.3 μ の乾式シリカ(SiO₂) (日本アエロジル(株)製“アエロジル”R-972) 1.0重量多をエナレングリコールスラリーとして添加した。既いて系内を徐々に減圧とし、1mmHg以下の減圧下で285℃の温度にしてエナレングリコールを留出し、4時間で反応を終了した。得られたポリマーは固有粘度0.618を有し、SiO₂ 1.0重量多を含有していた。(ポリエステル:A)

得た。該組成物を285℃で溶融押出し、60℃の冷却ドラム上にキャストし、無延伸シートとしたのち常法により長手方向3.5倍、幅方向3.5倍延伸し、やや弛緩しつつ215℃で熱処理し、厚み3 μ のポリエチレンテレフタレート2軸延伸フィルムを得た。得られたフィルムのヘイズは2.0%で静摩擦係数0.63、フィルム表面の平均粗さ0.018 μ 、フィルム表面最大粗さ0.20 μ 、絶縁破壊電圧545V/ μ と透明性、平担性、滑性、電気特性共に極めて優れていた。

実施例3 (実験例1~12)

実施例2のポリエステルAと同様の方法で乾式シリカの代りにポリエチレンテレフタレート100重量多に対し、平均粒径1.5 μ の炭酸カルシウムを20重量多含有するポリエステルを得た。(ポリエステル:D)

一方、平均粒径0.9 μ を有するカオリナイトを30重量多含有するポリエステルを得た。(ポリエステル:B)

これらのポリマーおよび実施例2で得られた

ポリエステル:Aと同様の方法で不活性粒子を添加しない固有粘度0.615のポリマーを得た。(ポリエステル:B)

ジメチルテレフタレート100重量多、エナレングリコール65重量多およびエステル交換触媒として酢酸カルシウム0.09重量多、重合触媒として三酸化アンチモン0.03重量多を加え、140~220℃の間で理論量のメタノールを留出させ、エステル交換反応を終了させた。既いて系内にジメチルフェニルホスホネート0.1重量多、亜リン酸0.03重量多を添加したのち常法に従つて重合反応を行ない、反応終了後PIRを20重量多添加し、約10分間の減圧乾燥を行ない、固有粘度0.609のポリマーを得た。(ポリエステル:C)

かくして得られたポリエステルA、ポリエステルB、ポリエステルCを混合しながら減圧乾燥後(170℃×2時間)、全体としてポリエステル100重量多、乾式シリカ0.3重量多、PIRのリン量0.05重量多からなる組成物を

ポリマーと各種リン化合物含有ポリマーを各々ブレンドし、実施例2と同様の方法で実験例1~12に示す組成物としフィルムを作成した。(表-1)

実験例1は滑性および絶縁破壊電圧に劣り、また実験例7はカオリナイトの添加量が上限を越えるため平担性および絶縁破壊電圧が劣っている。

実験例4、6は不活性粒子が添加されていないため滑性が大巾に低下している。

実験例5、11はフィルム中の添加リン化合物のリン量およびリン化合物の分子量が好ましくない例であり、滑性、絶縁破壊電圧の両方またはいずれかの特性が低下している。

実験例2、5、8、9、10、12は本発明の範囲になるものであり滑性、平担性、絶縁破壊電圧特性に優れていた。

表 1

実 験 例	組成 (ポリエステル100部当りに対する重量部)					非晶性 係 数	フィルム表面粗さ (μ)		フィルム 厚 さ (μ)	絶 縁 破壊電圧 (V/μ)
	不 活 性 成 分		リ ン 化 合 物							
	種 類	量	種 類	分子量	リン量					
(実施例1)	乾式シリカ	0.3	P I R	434	0.07	0.60	0.20	0.020	1.9	548
(実施例2)	乾式シリカ	0.3	P I R	434	0.05	0.63	0.20	0.018	2.0	545
(実施例3)	乾式シリカ	0.5	—	—	—	0.85	0.23	0.020	1.8	463
2	CaO ₂	0.1	P I R	434	0.01	0.72	0.30	0.028	2.8	555
3	カオリナイト	0.1	P I R	434	0.2	0.68	0.27	0.025	2.7	482
4	—	—	P I R	434	0.05	3.5	0.09	0.012	0.5	540
5	乾式シリカ	0.5	P I R	434	0.01	0.52	0.25	0.022	2.3	534
6	—	—	—	—	—	4.01	0.05	0.009	0.3	550
7	カオリナイト	3.0	P I R	434	0.01	0.39	0.35	0.040	4.9	443
8	乾式シリカ	0.5	フェニルグリソオキソナフタレート	382	0.01	0.65	0.25	0.025	2.1	530
9	乾式シリカ	0.5	トリシクロヘキシルホスフェート	344	0.01	0.70	0.27	0.026	2.0	521
10	乾式シリカ	0.3	ベンゾリザントリフェニルフォスファラン	352	0.01	0.74	0.26	0.024	1.9	514
11	カオリナイト	0.1	ジフェニルホスファイト	234	0.03	0.80	0.28	0.025	2.5	470
12	カオリナイト	0.1	P I R	434	0.01	0.71	0.27	0.026	2.3	531

